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INTERNAL REPORT

DERIVATION OF FORMULAS FOR EVALUATING THE STANDARD ERRORS IN B, C, AND N WHICH APPEAR IN THE FUNDAMENTAL EQUATION FOR THE BURNETT EXPERIMENT: $Z_r = (Z_o/P_o)N^r P_r$

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BRANCH Branch of Fundamental Research

PROJECT NO. 4335

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ABSTRACT

The method of treating a set of isothermally measured pressures P_o, P_1, P_2, ... , P_r, for a Burnett experiment, consists of expressing the compressibility factor isotherm of the gas in terms of a function of either P or ρ and evaluating the volume ratio, N, and the so-called virial coefficients by least squares solution. This report gives the method of least squares and its application to the fundamental equation for the Burnett experiment.

Formulas are given for evaluating the constants which appear in the equation $Z_r = (Z_o/P_o)N^r P_r$ together with formulas for calculating the standard deviation of a single $P_{r(obs)}$, the standard deviation of each of the constants evaluated, and the standard deviation of the compressibility factor.

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INTRODUCTION

The Helium Research Center is presently engaged in a critical examination of all of the thermodynamic data on helium that appear in the literature. The long-range objective is the development of a single equation of state for helium that will allow all of the thermodynamic properties to be calculated and will reproduce all of the data within the accuracy with which the data are known. A preliminary objective is to obtain the best values of second virial coefficients and to develop an equation that will reproduce the best values as a function of temperature.

The method of treating a set of isothermally measured pressures, P_o, P_1, P_2, ..., P_r, for a Burnett experiment, consists of expressing Z in terms of a function of either P or ρ and evaluating the constants by least squares solution. Associated with this function, the following errors are of interest: the standard deviation of a single $P_{r(obs)}$; the standard deviation of each of the constants evaluated; and the standard deviation of the function.

The purpose of this report is to present the method of least squares as applied to the fundamental equation for the Burnett experiment together with formulas which were derived for evaluating the best values for the constants and the above-mentioned errors.

METHOD OF OBTAINING THE LEAST SQUARES SOLUTION FOR THE CONSTANTS APPEARING IN THE EQUATION: $Z_r = (Z_o/P_o)N^r P_r$

The fundamental equation for the Burnett experiment is of the form

$$Z_r = (Z_o/P_o)N^r P_r \tag{1}$$

where N is the volume ratio of the Burnett apparatus; P_o is the initial starting pressure; r refers to the expansion number; P_r is the pressure after the $r^{\underline{th}}$ expansion; Z_r and Z_o are compressibility factors at P_r and P_o, respectively.

There are two series expansions which can be used for representing Z's: the Leiden expansion in powers of reciprocal volume, and the Berlin expansion in powers of pressure. We represented the compressibility factor isotherm as

$$Z_r = 1 + BP_r + CP_r^2 + \ldots \tag{2}$$

and

$$Z_o = 1 + BP_o + CP_o^2 + \ldots \tag{3}$$

and it was assumed that equations (2) and (3) could be truncated after the third virial coefficient. The Berlin expansion was chosen to represent the compressibility factor isotherm because all of the parameters appearing in equation (1) could be expressed in terms of the original observations.

Let the functional relationship between the variables, P_r and r, involving the three parameters N, B, and C, be

$$F = F(r, P_r, N, B, C) = 0 \tag{4}$$

Now because of random errors in the observed pressures, when $P_{r(obs)}$ is substituted in the above expression, F will not be exactly zero. Let F_r be the value of F when the observed values of r and P_r are substituted in equation (4). Thus,

$$F_r = F(r, P_{r(obs)}, N, B, C) \tag{5}$$

Now we assume that r is accurately known. Therefore, equation (4) may be solved for $P_{r(calc)}$ so that equation (4) is exactly satisfied. Thus,

$$F = F(r, P_{r(calc)}, N, B, C) = 0 \tag{6}$$

and $P_{r(calc)}$ is the correct solution of equation (6).

Now ΔP_r, the residual of P_r, is the difference between $P_{r(obs)}$ and $P_{r(calc)}$. This is not the true random error in the observed P_r because we do not know the true value of P_r. However, we can maximize the probability that ΔP_r is equal to the true random error and this is just what the principle of least squares does. The principle of least squares says that we maximize the probability that the ΔP_r's represent the true random errors by minimizing the sum of the squares of the weighted residuals. Thus, we should minimize the

function

$$R = \sum_{r=1}^{r} W_{P_{r(obs)}} (\Delta P_r)^2$$

$$= \sum_{r=1}^{r} W_{P_{r(obs)}} Y_i^2 \tag{7}$$

where ΔP_r is

$$\Delta P_r = Y_i = P_{r(obs)} - P_{r(calc)} \tag{8}$$

and evaluate B, C, and N so that

$$\left(\frac{\partial R}{\partial B}\right)_{r,\ P_{r(obs)},\ N,\ C} = 2\sum_{r=1}^{r} W_{P_{r(obs)}} Y_i \left(\frac{\partial Y_i}{\partial B}\right) = 0 \tag{9}$$

$$\left(\frac{\partial R}{\partial C}\right)_{r,\ P_{r(obs)},\ B,\ N} = 2\sum_{r=1}^{r} W_{P_{r(obs)}} Y_i \left(\frac{\partial Y_i}{\partial C}\right) = 0 \tag{10}$$

$$\left(\frac{\partial R}{\partial N}\right)_{r,\ P_{r(obs)},\ B,\ C} = 2\sum_{r=1}^{r} W_{P_{r(obs)}} Y_i \left(\frac{\partial Y_i}{\partial N}\right) = 0 \tag{11}$$

In equations (7), (9), (10), and (11), $W_{P_{r(obs)}}$ is the weight to be assigned to the observed P_r. If the P_r's all have the same precision index, then they will have the same weight and $W_{P_{r(obs)}} = 1$. If the P_r's do not all have the same precision index, then

$$W_{P_{r(obs)}} = \frac{L^2}{S^2_{P_{r(obs)}}} \tag{12}$$

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where L is a constant and $S^2_{P_{r(obs)}}$ is the variance of $P_{r(obs)}$.

In a particular problem, it may be necessary to assume $W_{P_{r(obs)}} = 1$ in the beginning. However, if this is done, the residuals, $Y_i = [P_{r(obs)} - P_{r(calc)}]$, should be examined to see if there is any statistical evidence for the residuals squared being a function of $P_{r(obs)}$. Any assumption as to the variance being a function of $P_{r(obs)}$ can always be checked by examining the residuals. In any event, $W_{P_{r(obs)}}$ is not a function of the constants to be evaluated.

In order to evaluate the constants, we need to linearize Y_i with respect to the undetermined constants. A truncated Taylor's series expansion was used to do this.

In a previous report (1)[3/], we show that the linearized normal

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3/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

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equations are expressible as

$$a_1 \; \Delta B + b_1 \; \Delta C + c_1 \; \Delta N = m_1 \tag{13}$$

$$a_2 \; \Delta B + b_2 \; \Delta C + c_2 \; \Delta N = m_2 \tag{14}$$

$$a_3 \; \Delta B + b_3 \; \Delta C + c_3 \; \Delta N = m_3 \tag{15}$$

Equations (13), (14), and (15) result from expanding Y_i, $(\partial Y_i/\partial B)$, $(\partial Y_i/\partial C)$, and $(\partial Y_i/\partial N)$ about the approximate solution Y_i^o, ignoring second and higher order derivatives. The linearized coefficients ΔB, ΔC, ΔN are defined as

$$\Delta B = B - B^o \tag{16}$$

$$\Delta C = C - C^o \tag{17}$$

$$\Delta N = N - N^o \tag{18}$$

where B, C, and N are our undetermined constants, and B^o, C^o, N^o are approximate values for these quantities.

The a's, b's, c's, and m's appearing in the normal equations are given to be (1).

$$a_1 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^{o^2} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial B^2}\right)^o \right] \tag{19}$$

$$a_2 = b_1 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial C}\right)^o + Y_i^o \left(\frac{\partial^2 Y_i}{\partial B \partial C}\right)^o \right] \tag{20}$$

$$a_3 = c_1 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial B}\right)^o \left(\frac{\partial Y_i}{\partial N}\right)^o + Y_i^o \left(\frac{\partial^2 Y_i}{\partial B \partial N}\right)^o \right] \tag{21}$$

$$b_2 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^{o\,2} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial C^2}\right)^o \right] \tag{22}$$

$$b_3 = c_2 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial C}\right)^o \left(\frac{\partial Y_i}{\partial N}\right)^o + Y_i^o \left(\frac{\partial^2 Y_i}{\partial C \partial N}\right)^o \right] \tag{23}$$

$$c_3 = \sum_{r=1}^{r} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_i}{\partial N}\right)^{o\,2} + Y_i^o \left(\frac{\partial^2 Y_i}{\partial N^2}\right)^o \right] \tag{24}$$

$$m_1 = - \sum_{r=1}^{r} W_{P_{r(obs)}} \; Y_i^o \left(\frac{\partial Y_i}{\partial B}\right)^o \tag{25}$$

$$m_2 = - \sum_{r=1}^{r} W_{P_{r(obs)}} \; Y_i^o \left(\frac{\partial Y_i}{\partial C}\right)^o \tag{26}$$

$$m_3 = - \sum_{r=1}^{r} W_{P_{r(obs)}} \; Y_i^o \left(\frac{\partial Y_i}{\partial N}\right)^o \tag{27}$$

and

$$\left(\frac{\partial Y_i}{\partial B}\right)^o = \frac{(\partial F/\partial B)^o}{(\partial F/\partial P_{r(calc)})^o} \tag{28}$$

$$\left(\frac{\partial Y_i}{\partial C}\right)^o = \frac{(\partial F/\partial C)^o}{(\partial F/\partial P_{r(calc)})^o} \tag{29}$$

$$\left(\frac{\partial Y_i}{\partial N}\right)^o = \frac{(\partial F/\partial N)^o}{(\partial F/\partial P_{r(calc)})^o} \tag{30}$$

$$\left(\frac{\partial^2 Y_i}{\partial B^2}\right)^o = \left[\frac{(\partial^2 F/\partial B^2)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{2(\partial^2 F/\partial B\partial P_{r(calc)})^o(\partial F/\partial B)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial B)^{o^2}\ (\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \tag{31}$$

$$\left(\frac{\partial^2 Y_i}{\partial C^2}\right)^o = \left[\frac{(\partial^2 F/\partial C^2)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{2(\partial^2 F/\partial C\partial P_{r(calc)})^o(\partial F/\partial C)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial C)^{o^2}\ (\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \tag{32}$$

$$\left(\frac{\partial^2 Y_i}{\partial N\partial B}\right)^o = \left(\frac{\partial^2 Y_i}{\partial B\partial N}\right)^o = \left[\frac{(\partial^2 F/\partial N\partial B)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{(\partial^2 F/\partial B\partial P_{r(calc)})^o(\partial F/\partial N)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} - \frac{(\partial F/\partial B)^o(\partial^2 F/\partial P_{r(calc)}\partial N)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial B)^o(\partial F/\partial N)^o(\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \tag{33}$$

$$\left(\frac{\partial^2 Y_i}{\partial N \partial C}\right)^o = \left(\frac{\partial^2 Y_i}{\partial C \partial N}\right)^o = \left[\frac{(\partial^2 F/\partial N \partial C)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{(\partial^2 F/\partial C \partial P_{r(calc)})^o (\partial F/\partial N)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} - \frac{(\partial F/\partial C)^o (\partial^2 F/\partial P_{r(calc)} \partial N)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial C)^o (\partial F/\partial N)^o (\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \tag{34}$$

$$Y_i^o = [P_{r(obs)} - P_{r(calc)}]^o \tag{35}$$

$$\left(\frac{\partial^2 Y_i}{\partial N^2}\right)^o = \left[\frac{(\partial^2 F/\partial N^2)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{2(\partial^2 F/\partial N \partial P_{r(calc)})^o (\partial F/\partial N)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial N)^{o^2} (\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \tag{36}$$

$$\left(\frac{\partial^2 Y_i}{\partial C \partial B}\right)^o = \left(\frac{\partial^2 Y_i}{\partial B \partial C}\right)^o = \left[\frac{(\partial^2 F/\partial C \partial B)^o}{(\partial F/\partial P_{r(calc)})^o} - \frac{(\partial^2 F/\partial B \partial P_{r(calc)})^o (\partial F/\partial C)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} - \frac{(\partial F/\partial B)^o (\partial^2 F/\partial P_{r(calc)} \partial C)^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^2} + \frac{(\partial F/\partial B)^o (\partial F/\partial C)^o (\partial^2 F/\partial P^2_{r(calc)})^o}{\left[(\partial F/\partial P_{r(calc)})^o\right]^3}\right] \tag{37}$$

Now in order to evaluate the solutions of our linearized normal equations, we need values of first and second derivatives of the function, F,

$$F = F(r, P_{r(calc)}, N, B, C) = 0 \qquad (6)$$

or

$$F = Z_{r(calc)} - (Z_o/P_o)N^r P_{r(calc)} = 0$$

$$= 1 + BP_{r(calc)} + CP^2_{r(calc)} - \left(\frac{1 + BP_o + CP_o^2}{P_o}\right)N^r P_{r(calc)} = 0 \qquad (38)$$

These derivatives are:

$$\left(\frac{\partial F}{\partial B}\right) = P_{r(calc)} (1 - N^r)$$

$$\left(\frac{\partial F}{\partial C}\right) = P_{r(calc)}\left[P_{r(calc)} - N^r P_o\right]$$

$$\left(\frac{\partial F}{\partial N}\right) = - r(Z_o/P_o)N^{r-1} P_{r(calc)}$$

$$\left(\frac{\partial F}{\partial P_{r(calc)}}\right) = B + 2CP_{r(calc)} - (Z_o/P_o)N^r$$

$$\left(\frac{\partial^2 F}{\partial B^2}\right) = 0$$

$$\left(\frac{\partial^2 F}{\partial C^2}\right) = 0$$

$$\left(\frac{\partial^2 F}{\partial N^2}\right) = -r(r-1)(Z_o/P_o)N^{r-2}\, P_{r(calc)}$$

$$\left(\frac{\partial^2 F}{\partial P^2_{r(calc)}}\right) = 2C$$

$$\left(\frac{\partial^2 F}{\partial C \partial B}\right) = 0$$

$$\left(\frac{\partial^2 F}{\partial N \partial B}\right) = - r\, N^{r-1}\, P_{r(calc)}$$

$$\left(\frac{\partial^2 F}{\partial N \partial C}\right) = - r\, N^{r-1}\, P_o\, P_{r(calc)}$$

$$\left(\frac{\partial^2 F}{\partial P_{r(calc)} \partial B}\right) = 1 - N^r$$

$$\left(\frac{\partial^2 F}{\partial P_{r(calc)} \partial C}\right) = 2P_{r(calc)} - N^r\, P_o$$

$$\left(\frac{\partial^2 F}{\partial P_{r(calc)} \partial N}\right) = - r\, (Z_o/P_o)N^{r-1}$$

$$\left(\frac{\partial^2 F}{\partial N \partial P_{r(calc)}}\right) = \left(\frac{\partial^2 F}{\partial P_{r(calc)} \partial N}\right)$$

$$\left(\frac{\partial^2 F}{\partial B \partial P_{r(calc)}}\right) = \left(\frac{\partial^2 F}{\partial P_{r(calc)} \partial B}\right)$$

$$\left(\frac{\partial^2 F}{\partial C \partial P_{r(calc)}}\right) = \left(\frac{\partial^2 F}{\partial P_{r(calc)} \partial C}\right)$$

Now in evaluating the best values for B, C, and N, we must solve the linearized normal equations by an iterative procedure. When we have the correct solutions, equations (13), (14), and (15) will be satisfied exactly. The solutions to equations (13), (14), and (15) are (1)

$$D_o \Delta B = D_1 m_1 + D_2 m_2 + D_3 m_3 \tag{39}$$

$$D_o \Delta C = D_4 m_1 + D_5 m_2 + D_6 m_3 \tag{40}$$

$$D_o \Delta N = D_7 m_1 + D_8 m_2 + D_9 m_3 \tag{41}$$

where

$$D_1 = b_2 c_3 - b_3 c_2 \tag{42}$$

$$D_4 = D_2 = b_3 c_1 - b_1 c_3 \tag{43}$$

$$D_7 = D_3 = b_1 c_2 - b_2 c_1 \tag{44}$$

$$D_5 = a_1 c_3 - a_3 c_1 \tag{45}$$

$$D_8 = D_6 = a_2 c_1 - a_1 c_2 \tag{46}$$

$$D_9 = a_1 b_2 - a_2 b_1 \tag{47}$$

$$D_o = D_1 a_1 + D_2 a_2 + D_3 a_3 \tag{48}$$

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EXPRESSIONS FOR DETERMINING VARIANCES AND COVARIANCES OF THE CONSTANTS EVALUATED

We now proceed to evaluate the variances of the constants and all of the covariances. To do this, we apply the law for the "Propagation of Errors" (3, 4). This law states that if we have a function or quantity, say Q, that is a function of the independently observed quantities y_1, y_2, ... , then the variance of the quantity Q, is given as

$$S_Q^2 = \sum_{i=1}^{n} \left(\frac{\partial Q}{\partial y_{i(obs)}} \right)^2 S^2_{y_{i(obs)}} \tag{49}$$

where S_Q^2 is the variance of Q and $S^2_{y_{i(obs)}}$ is the variance of $y_{i(obs)}$. Extracting the square root of the variance, we obtain a value on the same scale as the original measurements. This value, S_Q, is called the standard error or the standard deviation of Q.

Now suppose we evaluate the variance of the constant B. The value of B which we have evaluated is a function of all of the observed P_r's and r's. Since we have assumed that r is accurately known, then the expression for the variance of B is given by the equation

$$S_B^2 = \sum_{r=1}^{r} \left(\frac{\partial B}{\partial P_{r(obs)}} \right)^2 \cdot S^2_{P_{r(obs)}} \tag{50}$$

and there will be an equation similar to equation (50) for determining the variance of C and the variance of N.

To evaluate equation (50), we must evaluate $(\partial B/\partial P_{r(obs)})$ for each $P_{r(obs)}$, multiply this quantity by $S_{P_{r(obs)}}$, square the

product and then sum the product over r from 1 to r for the r expansions.

In a previous report (2), we have outlined the details for evaluating the variances and all of the covariances of the constants evaluated.

For our particular problem, these variances and covariances are determined from the following relations (2):

$$S_B^2 = \frac{L^2}{D_o^2}\left[\begin{aligned} & D_1^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^{o^2} + D_2^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^{o^2} \\ & + D_3^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial N}\right)^{o^2} + 2D_1D_2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^{o}\left(\frac{\partial Y_i}{\partial C}\right)^{o} \\ & + 2D_1D_3 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^{o}\left(\frac{\partial Y_i}{\partial N}\right)^{o} + 2D_2D_3 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^{o}\left(\frac{\partial Y_i}{\partial N}\right)^{o} \end{aligned}\right] \qquad (51)$$

$$S_C^2 = \frac{L^2}{D_o^2}\left[\begin{aligned} & D_4^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^{o^2} + D_5^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^{o^2} \\ & + D_6^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial N}\right)^{o^2} + 2D_4D_5 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^{o}\left(\frac{\partial Y_i}{\partial C}\right)^{o} \\ & + 2D_4D_6 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)^{o}\left(\frac{\partial Y_i}{\partial N}\right)^{o} + 2D_5D_6 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)^{o}\left(\frac{\partial Y_i}{\partial N}\right)^{o} \end{aligned}\right] \qquad (52)$$

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$$S_N^2 = \frac{L^2}{D_o^2} \left[\begin{aligned} & D_7^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)_o^2 + D_8^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)_o^2 \\ & + D_9^2 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial N}\right)_o^2 + 2D_7D_8 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)_o \left(\frac{\partial Y_i}{\partial C}\right)_o \\ & + 2D_7D_9 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)_o \left(\frac{\partial Y_i}{\partial N}\right)_o + 2D_8D_9 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)_o \left(\frac{\partial Y_i}{\partial N}\right)_o \end{aligned} \right] \tag{53}$$

$$S_{BC}^2 = \frac{L^2}{D_o^2} \left[\begin{aligned} & D_1D_4 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)_o^2 + D_2D_5 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)_o^2 \\ & + D_3D_6 \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial N}\right)_o^2 \\ & + (D_2D_4 + D_1D_5) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)_o \left(\frac{\partial Y_i}{\partial C}\right)_o \\ & + (D_1D_6 + D_3D_4) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial B}\right)_o \left(\frac{\partial Y_i}{\partial N}\right)_o \\ & + (D_2D_6 + D_3D_5) \sum_{r=1}^{r} W_{P_{r(obs)}} \left(\frac{\partial Y_i}{\partial C}\right)_o \left(\frac{\partial Y_i}{\partial N}\right)_o \end{aligned} \right] \tag{54}$$

$$S_{BN}^2 = \frac{L^2}{D_o^2}\left[\begin{array}{l} D_1D_7\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial B}\right)_o^2 + D_2D_8\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial C}\right)_o^2 \\ + D_3D_9\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial N}\right)_o^2 \\ + (D_1D_8 + D_2D_7)\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial B}\right)_o\left(\frac{\partial Y_i}{\partial C}\right)_o \\ + (D_1D_9 + D_3D_7)\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial B}\right)_o\left(\frac{\partial Y_i}{\partial N}\right)_o \\ + (D_2D_9 + D_3D_8)\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial C}\right)_o\left(\frac{\partial Y_i}{\partial N}\right)_o \end{array}\right] \tag{55}$$

$$S_{CN}^2 = \frac{L^2}{D_o^2}\left[\begin{array}{l} D_4D_7\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial B}\right)_o^2 + D_5D_8\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial C}\right)_o^2 \\ + D_6D_9\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial N}\right)_o^2 \\ + (D_4D_8 + D_5D_7)\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial B}\right)_o\left(\frac{\partial Y_i}{\partial C}\right)_o \\ + (D_4D_9 + D_6D_7)\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial B}\right)_o\left(\frac{\partial Y_i}{\partial N}\right)_o \\ + (D_5D_9 + D_6D_8)\sum_{r=1}^{r} W_{P_{r(obs)}}\left(\frac{\partial Y_i}{\partial C}\right)_o\left(\frac{\partial Y_i}{\partial N}\right)_o \end{array}\right] \tag{56}$$

We have indicated that the solutions to our linearized normal equations are to be solved by an iterative procedure. When we have the correct solutions, equations (13), (14), and (15) will be satisfied exactly. Therefore, once we have determined the best values for B, C, and N, the remaining questions to be answered are: (1) what is the variance of the calculated P_r's and any other calculated P that reduces the fundamental equation for the Burnett experiment to an exact identity?; and (2) what is the variance of the compressibility factor?

EVALUATION OF THE VARIANCE OF THE $P_{r(calc)}$'s AND ANY OTHER CALCULATED P THAT REDUCES F TO ZERO

Because of random errors in the observed pressures, equation (4) will not be satisfied exactly when the observed P_r's are substituted into this equation. Hence, we need to evaluate the variance of the calculated P_r's which will reduce F to zero for each observed r value. We do this in the following way: $P_{r(calc)}$ is a function of the observed r's and, through the constants evaluated, is a function of all of the observed P_r's. To evaluate the variance of $P_{r(calc)}$, we apply the law for the "Propagation of Errors" (3, 4). From equation (49), we see that this involves evaluation of the quantity

$$S^2_{P_{r(calc)}} = \sum_{r=1}^{r} \left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right)^2 S^2_{P_{r(obs)}} \tag{57}$$

Now in order to evaluate equation (57), we must evaluate $[\partial P_{r(calc)}/\partial P_{r(obs)}]$ for each $P_{r(obs)}$, multiply this quantity by

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[illegible]

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[illegible]

$S_{P_{r(obs)}}$, square the product and then sum the product over all of the observed P_r's. $[\partial P_{r(calc)}/\partial P_{r(obs)}]$ can be determined from equation (6). Suppose we differentiate equation (6) with regard to $P_{r(obs)}$, holding r constant

$$\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N}\left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right) + \left(\frac{\partial F}{\partial B}\right)_{r,C,N,P_{r(calc)}}\left(\frac{\partial B}{\partial P_{r(obs)}}\right) + \left(\frac{\partial F}{\partial C}\right)_{r,B,N,P_{r(calc)}}\left(\frac{\partial C}{\partial P_{r(obs)}}\right) + \left(\frac{\partial F}{\partial N}\right)_{r,B,C,P_{r(calc)}}\left(\frac{\partial N}{\partial P_{r(obs)}}\right)\right] = 0 \qquad (58)$$

or

$$\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N}\left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right) = -\left[\left(\frac{\partial F}{\partial B}\right)_{r,C,N,P_{r(calc)}}\left(\frac{\partial B}{\partial P_{r(obs)}}\right) + \left(\frac{\partial F}{\partial C}\right)_{r,B,N,P_{r(calc)}}\left(\frac{\partial C}{\partial P_{r(obs)}}\right) + \left(\frac{\partial F}{\partial N}\right)_{r,B,C,P_{r(calc)}}\left(\frac{\partial N}{\partial P_{r(obs)}}\right)\right] \qquad (59)$$

and solving equation (59) for $[\partial P_{r(calc)}/\partial P_{r(obs)}]$, we get

$$\left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right) = - \left[\frac{\left(\frac{\partial F}{\partial B}\right)_{r,C,N,P_{r(calc)}} \left(\frac{\partial B}{\partial P_{r(obs)}}\right) + \left(\frac{\partial F}{\partial C}\right)_{r,B,N,P_{r(calc)}} \left(\frac{\partial C}{\partial P_{r(obs)}}\right) + \left(\frac{\partial F}{\partial N}\right)_{r,B,C,P_{r(calc)}} \left(\frac{\partial N}{\partial P_{r(obs)}}\right)}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N}} \right] \tag{60}$$

Multiplying equation (60) by $S_{P_{r(obs)}}$, squaring the product, and summing over all of the observed P_r's, we get

$$S^2_{P_{r(calc)}} = \left[\frac{S_B^2 \left(\frac{\partial F}{\partial B}\right)^2_{r,C,N,P_{r(calc)}} + 2S^2_{BC} \left(\frac{\partial F}{\partial B}\right)_{r,C,N,P_{r(calc)}} \left(\frac{\partial F}{\partial C}\right)_{r,B,N,P_{r(calc)}} + S_C^2 \left(\frac{\partial F}{\partial C}\right)^2_{r,B,N,P_{r(calc)}} + 2S^2_{BN} \left(\frac{\partial F}{\partial B}\right)_{r,C,N,P_{r(calc)}} \left(\frac{\partial F}{\partial N}\right)_{r,B,C,P_{r(calc)}} + S_N^2 \left(\frac{\partial F}{\partial N}\right)^2_{r,B,C,P_{r(calc)}} + 2S^2_{CN} \left(\frac{\partial F}{\partial C}\right)_{r,B,N,P_{r(calc)}} \left(\frac{\partial F}{\partial N}\right)_{r,B,C,P_{r(calc)}}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^2_{r,B,C,N}} \right] \tag{61}$$

from which we can evaluate the (n-1) values of $S^2_{P_{r(calc)}}$ corresponding to the observed r's.

Now we ask ourselves the question: how do we calculate the variance of any other calculated P that exactly satisfies equation (6)? In order to answer this question, we must find a value of r, say r_P, which exactly satisfies the equation

$$Z_{P_{(calc)}} \equiv (Z_o/P_o)\, N^{r_P}\, P_{(calc)} \tag{62}$$

where

$$Z_{P_{(calc)}} = 1 + BP_{(calc)} + CP^2_{(calc)} \tag{63}$$

Now suppose we have evaluated B, C, and N by some means or other. Then rearranging equation (62) as

$$N^{r_P} = \frac{Z_{P_{(calc)}}}{(Z_o/P_o)\, P_{(calc)}} \tag{64}$$

and taking natural logarithms of equation (64), we get

$$r_P = \frac{\ln Z_{P_{(calc)}} - \ln (Z_o/P_o) - \ln P_{(calc)}}{\ln N} \tag{65}$$

from which we can evaluate r_P, and r_P is just the expansion number corresponding to $P_{(calc)}$.

To evaluate the variance of $P_{(calc)}$, we must evaluate the quantity

$$S^2_{P_{(calc)}} = \sum_{r=1}^{r} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)^2 \cdot S^2_{P_{r(obs)}} \qquad (66)$$

Now in order to evaluate equation (66), we return to equation (61), where the terms involving derivatives of F are to be evaluated for $P_{(calc)}$, ${}^{r}P$.

EXPRESSION FOR EVALUATING THE VARIANCE OF THE COMPRESSIBILITY FACTOR

We now proceed to evaluate the variance of Z. To do this we apply the law for the "Propagation of Errors." Now $Z_{(calc)}$ is a function of r_P and, through the constants evaluated, is a function of all of the original $P_{r(obs)}$'s. From our equation,

$$Z_{P(calc)} = 1 + BP_{(calc)} + CP^2_{(calc)} , \qquad (63)$$

where $P_{(calc)}$ is any calculated P which exactly satisfies equation (6), we see that the variance in $Z_{P_{(calc)}}$, as given by equation (49), involves evaluation of the quantity

$$S^2_{Z_{P_{(calc)}}} = \sum_{r=1}^{r} \left(\frac{\partial Z_{P_{(calc)}}}{\partial P_{r(obs)}}\right)^2 \cdot S^2_{P_{r(obs)}} \qquad (67)$$

In order to evaluate equation (67), we must evaluate $[\partial Z_{P_{(calc)}}/\partial P_{r(obs)}]$ for each $P_{r(obs)}$, multiply this quantity by $S_{P_{r(obs)}}$, square the product, and then sum the product over all of the observed P_r's. When we do this, we get

$$S^2_{Z_{P_{(calc)}}} = \left[\begin{array}{l} B^2 S^2_{P_{(calc)}} + 4C^2P^2_{(calc)} S^2_{P_{(calc)}} + P^2_{(calc)} S^2_B \\ + P^4_{(calc)} S^2_C + 4BCP_{(calc)} S^2_{P_{(calc)}} + 2BP_{(calc)} S^2_{B,P_{(calc)}} \\ \\ + 2BP^2_{(calc)} S^2_{C,P_{(calc)}} + 4CP^2_{(calc)} S^2_{B,P_{(calc)}} \\ + 4CP^3_{(calc)} S^2_{C,P_{(calc)}} + 2P^3_{(calc)} S^2_{BC} \end{array}\right] \tag{68}$$

The terms $S^2_{B,P_{(calc)}}$ and $S^2_{C,P_{(calc)}}$, which appear in equation (68), are defined as

$$S^2_{B,P_{(calc)}} = \sum_{r=1}^{r} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial B}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} \tag{69}$$

$$S^2_{C,P_{(calc)}} = \sum_{r=1}^{r} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial C}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} \tag{70}$$

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and these quantities are to be evaluated from equations (69) and (70), which we proceed to do.

$[\partial P_{(calc)}/\partial P_{r(obs)}]$ can be determined from equation (60), where the terms involving derivatives of F are to be evaluated for $P_{(calc)}$, r_P. Multiplying equation (60) by $(\partial B/\partial P_{r(obs)})\ S^2_{P_{r(obs)}}$ and summing over all of the observed P_r's, we get

$$\sum_{r=1}^{r} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial B}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} = S^2_{B,P_{(calc)}} = -\left[\frac{\left(\frac{\partial F}{\partial B}\right)_{r_P,C,N,P_{(calc)}} S^2_B + \left(\frac{\partial F}{\partial C}\right)_{r_P,B,N,P_{(calc)}} S^2_{BC} + \left(\frac{\partial F}{\partial N}\right)_{r_P,B,C,P_{(calc)}} S^2_{BN}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P,B,C,N}}\right] \quad (71)$$

Multiplying equation (60) by $(\partial C/\partial P_{r(obs)})\ S^2_{P_{r(obs)}}$ and then summing over all of the observed P_r's, we get

$$\sum_{r=1}^{r} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial C}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} = S^2_{C,P_{(calc)}} = -\left[\frac{\left(\frac{\partial F}{\partial B}\right)_{r_P,C,N,P_{(calc)}} S^2_{BC} + \left(\frac{\partial F}{\partial C}\right)_{r_P,B,N,P_{(calc)}} S^2_{C} + \left(\frac{\partial F}{\partial N}\right)_{r_P,B,C,P_{(calc)}} S^2_{CN}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P,B,C,N}}\right] \quad (72)$$

Therefore, the use of equations (71) and (72) in equation (68) will enable the variance of a calculated Z_P, $S^2_{Z_{P(calc)}}$ to be determined.

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